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Piezoresistive effect in epoxy-graphite composites

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Abstract

In this work, we investigate the piezoresistive response of epoxy-graphite composites. A resistive thick-film Wheatstone bridge is deposited by screen-printing onto a beam, a weight is then applied on the tip of the beam and the resulting electrical signal response is recorded, allowing the calculation of the gauge factor. The characterization was made at room temperature, 65°C and 100°C for different matrixes (epoxies with different glass transition temperatures, T_g), substrates (alumina and aluminum) and particles sizes (4 µm and 15 µm). The creep of the signal in time and temperature was also observed. The present work shows also the tremendous effect of T_g on piezoresistive behavior: the high T_g epoxy demonstrating better stability in time and temperature than the other one.

Keywords: piezoresistivity; epoxy-graphite composite; creep

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1. Introduction

Percolative materials find increasing use in industrial applications. For instance, thick-film resistors, which essentially consist of conductive oxide nanopowder in an insulating glassy matrix forming a paste and can be printed on various substrates [1], are used in electronic circuits and may be applied to sensors for mechanical and chemical quantities and temperature. Although these materials are of great interest for integrating sensing functions in high-reliability ceramic [2,3] and metal [4] devices, variants having lower processing temperatures compatible with organic substrates such as printed circuit boards (PCBs) are also sought for a wider range of applications [5,6]. From this perspective, the use of polymer/graphite composites featuring good processability and low-cost materials is very promising. Several properties of the material used, such as mechanical or electrical (depending on the type of sensor) must be therefore considered.

Nomenclature

T_g	glass transition temperature
GF, GF_L, GF_T	gauge factor, longitudinal (GF_L) and transverse (GF_T)
CTE	coefficient of thermal expansion

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In a previous study [7], we studied the conductivity properties of epoxy-graphite composites, regarding particle size and T_g effects, finally leading to the manufacture of micro-heaters based on these pastes. To continue the characterization of our pastes, we examined the piezoresistive behavior, which is of high interest for mechanical sensors, expanding on the preliminary version of this work [8]. Piezoresistivity has already been studied for ceramic [9,10] and polymer [6] thick-films resistors. However it has also been demonstrated that the effects depends strongly on the conductive properties of the filler [9]. As little work has been done concerning standard graphite (i.e. with an ellipsoidal shape), most of the literature dealing with graphite fibers or expanded graphite [11,12], we endeavored in this study to investigate the piezoresistive response of thick-film epoxy-graphite composite. The characterization was completed by the study of the creep of our beams in temperature.

2. Experimental

Test beams were produced using the screen-printing process. Different resistive pastes are deposited on the substrate, in a Wheatstone bridge configuration. For testing, a weight is then applied on the tip of the beam and the resulting electrical signal response is recorded, leading, after calculation, to the gauge factor (longitudinal and transverse). The particle size effect was investigated. Two kinds of graphite were tested as filler: KS4 and KS15. Both variants have an ellipsoidal shape and come from Timcal, Switzerland; KS4 (resp. KS15) meaning that 95% of the particles have a large axis smaller than 4 µm (resp. 15 µm). Two epoxies were also tested as matrix for the composites; they were chosen with different T_g values, in order to see the impact in creep stability. Table 1 sums up the characteristics of these epoxies. Pastes were made in each case for different volume fractions of filler: 10%, 12%, 15% and 20% in order to change the conductivity of the composite and observe the corresponding change in the piezoresistive response. Measurements were made at room temperature, 65°C and 100°C for both matrixes. By increasing the temperature, we know that thermal expansion of the composite will conflict with that of the substrate, even more drastically above T_g. Therefore, we decided to produce beams using two kinds of substrates with different CTEs: alumina and aluminum (cf. Table 2). Thermal characterization of these materials was performed using an optical dilatometer Misura ODLT 1200-30, from Expert System Solutions.

The gauge factor is defined as:

$$GF = (\Delta R/R)/(\Delta l/l) = (\Delta R/R)/\varepsilon \qquad (1)$$

where ($\Delta R/R$) is the relative change in resistance and ε the strain with $\varepsilon = \Delta l/l$

GF_L is the case where the current flows along the length of the beam (i.e. the current is parallel to the applied strain) and GF_T where the current flows along the width of the beam (i.e. current perpendicular to the applied strain). Both factors were determined in our experiments. However only the GF_L are discussed here, the effect being the same for GF_T but the relative error is higher due to a lower response. Finally, the creep of the signal vs. time was observed at different temperatures using the same beams. Measurements were made at 25°C, 40°C, 50°C, 60°C, 70°C, 80°C and 90°C for one complete cycle (unloaded/loaded/unloaded).

Table 1. Main properties of epoxy resins (supplier data)

Name	Supplier	T_g (°C)	Curing Schedule
Epotek 377	PolyScience AG	≈ 90	2h@150°C
Martens Plus	Swiss Composite	≈ 200	24h@100°C + 15h@230°C

Table 2. Main properties of alumina and aluminum substrates (supplier data)

Type	**Alumina**	**Aluminum**
Supplier	Kyocera, Japan	Metallica, Switzerland
Reference	A-476 (96% pure alumina)	AW-6082, rolled
Thickness [mm]	0.635	0.8
Strain at resistor	0.027	0.054
Young's Modulus [GPa]	315	69
$CTE_{theoretical}$ [10^{-6}/°C]	7.2	23.4
Insulator	-	Same epoxy as resistor + silica powder
Conductors / resistor terminations	Thick-film Au ink, ESL 8837, fired 850°C 10 min	Conductive epoxy-Ag adhesive, Epotecny E212, 5 min at 150°C

3. Results

3.1. Substrate characterization

Both substrates were characterized using an optical dilatometer. Measurements were done from 25°C to 140°C at 10°C/min. Fig 1.a presents the results that were obtained for the thermal expansion. As expected, aluminum exhibits a higher thermal expansion than alumina. Although not perfect, aluminum will ergo restrain less the epoxy in its expansion (see Fig 1.b). One will notice the particular shape of the epoxy thermal expansion curve. A shrinkage can be observed around 100°C. This can be explained by residual stress inside the matrix in the T_g range, probably coming from the curing: when the epoxy reaches T_g, it becomes plastic and relaxes [13].

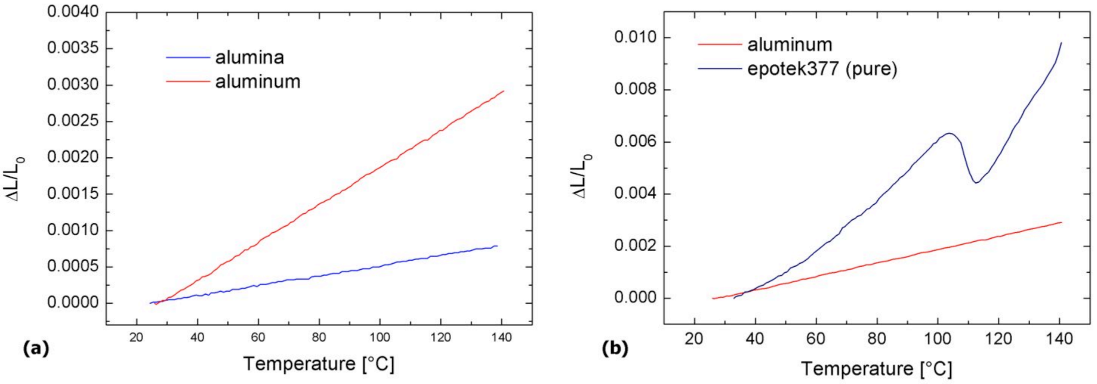

Fig 1. Comparison of the thermal expansion of alumina vs. aluminum substrates (a), and aluminum vs. pure Epotek 377 (b)

These curves allow the calculation of the coefficient of thermal expansion (CTE), which corresponds to the slope. In the previously defined temperature range, we experimentally found that alumina has a CTE of 6.9 x 10^{-6}/°C and aluminum 25.8 × 10^{-6}/°C. These values are in agreement with the suppliers' data (see Table 2).

3.2. Piezoresistive behavior

A first series of experiments was made on alumina beams to determine the particle size effect on piezoresistivity. Fig 2a reports the results of the GF_L at room temperature vs. volume fraction for KS4 and KS15, the matrix being the epoxy Epotek 377. A higher resistivity is linked to a higher gauge factor [9]. At the same volume fraction, smaller particles should create more tunnel junctions, hence smaller resistivity and gauge factor. This is not the case here: the results show that with the smaller particles, the gauge factor is somewhat higher. For a better understanding of the phenomenon, Fig 2.b presents the results of piezoresistivity vs. resistivity. Indeed, theoretically, we expect the piezoresistivity to increase linearly with the logarithm of the resistivity; we therefore replot these results as a function of the resistivity on a logarithmic scale. This is verified for both series, KS4 and KS15, in the lower resistivity range. In this representation of the piezoresistivity as a function of the resistivity, we would expect the two fillers to display identical values of the gauge factor, with the smaller filler eventually transitioning to a constant value at lower resistivity values than KS15. Here, although the values are indeed similar, we observe the opposite behavior. This can be explained by several aspects. First, both fillers are very close in size. Moreover, the theory mainly applies for spherical particles, which is not our case here: the aspect ratio of these particles was determined to be 2.6 for KS4 and 3.7 for KS15 [14]. Higher aspect ratios are supposed to lead to smaller gauge factors, which is what is observed experimentally here. In addition, there are strong indications that percolation in graphite is strongly influenced by debris that are much smaller than the primary particles [14], which also may explain the small observed differences between both fillers.

Fig. 3 presents the results on aluminum substrate. The tendency is the same as on alumina substrate. As piezoresistivity depends strongly on the filler this is quite understandable. We can also notice that the GF_L values are slightly higher.

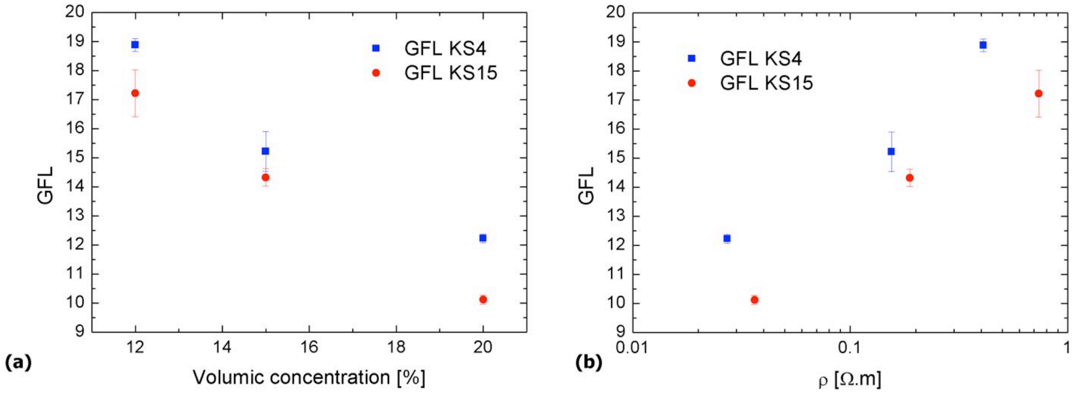

Fig 2. Effect of particle size on the GF$_L$ vs. graphite volumic concentration (a) and vs. resistivity (b) (substrate: alumina, matrix: Epotek 377, particles: KS4 and KS15)

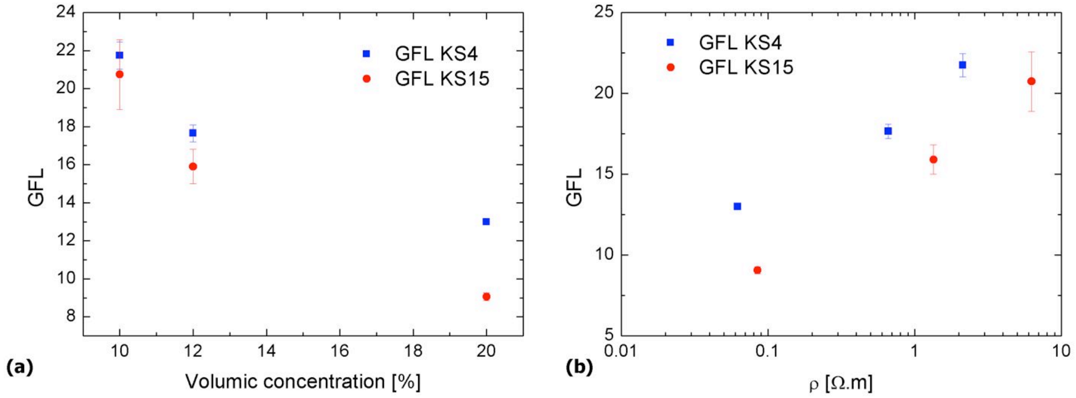

Fig 3. Effect of particle size on the GFL vs. graphite volumic concentration (a) and vs. resistivity (b) (substrate: aluminum, matrix: Epotek 377, particles: KS4 and KS15)

A second series of experiments was performed in order to see the impact of matrix thermo-mechanical stability on the samples. The gauge factor was calculated at room temperature, 65°C and 100°C. The corresponding results are reported in Fig 4. When the temperature is increased and reaches the range of T_g, several effects are in competition: increased thermal expansion of the epoxy in the z direction, compressive stress of the resistor in the xy plane, and decreased matrix stiffness. Due to high differences in the Young's Modulus between matrix and graphite, most of the mechanical strain is taken up by the matrix, this strain amplification leading to an increase of the gauge factor values [15]. With the high T_g epoxy, this effect is shifted: strains and matrix relaxation effects are lower, leading to an improved stability. In parallel to that, GF_L values were compared for samples using Epotek 377 as a matrix on alumina and aluminum. Measurements were not possible at 100°C for aluminum substrate for instability reasons, only the results for room temperature and 65°C are reported in Fig 5. We can see that the values change drastically on aluminum with temperature. Indeed, as the CTE of aluminum is higher than that of alumina, the strain mismatch with the graphite-epoxy composite is lower, altering the effects described above.

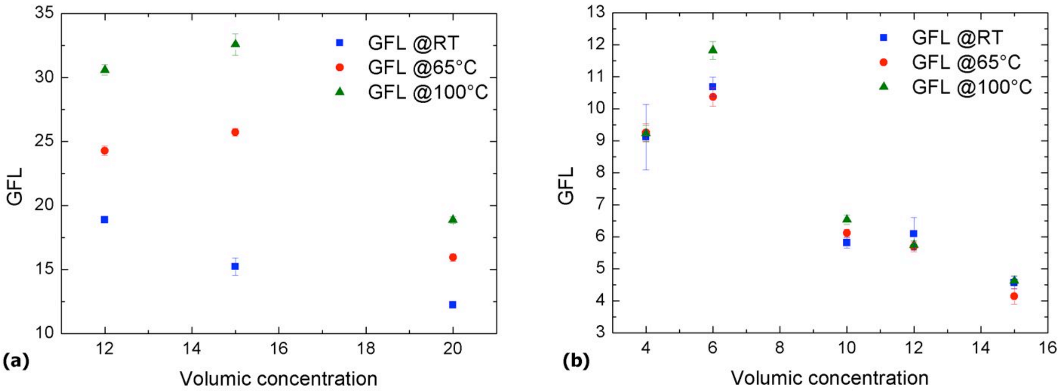

Fig 4. Longitudinal gauge factor at RT, 65°C and 100°C vs. graphite (KS4) volumic concentration for Epotek 377 (a) and Martens Plus (b) on alumina substrate

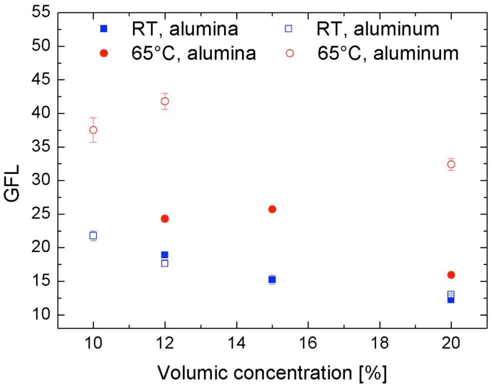

Fig 5. Longitudinal gauge factor at RT and 65°C vs. graphite (KS4) volumic concentration for Epotek 377 on alumina and aluminum substrates

3.3. Study of the piezoresistivity creep

Using the same beam, the creep of the signal in time was observed for one complete cycle: unloaded/loaded/unloaded. Fig 6 presents the curves obtained at 12% vol. graphite KS15 for the two epoxies at 25°C, 50°C and 80°C, on alumina substrate. When the temperature is raised close to the T_g of the Epotek 377, the material is disturbed due to higher thermal expansion of the matrix and relaxation effects, leading to strong instabilities (drifts) of the signal and higher GF_L values. Another possibility might be a low adhesion between matrix and filler, leading to instabilities. Indeed, graphite is non polar and shows poor chemical affinity with the epoxy and tends therefore to agglomerate [16]. This is one of the reasons for functionalizing graphite fibers for mechanical applications, for instance through oxidation, the creation of –OH groups on the graphite surface enhancing bonds with the polar groups of the epoxy [18-20]. On the contrary, carbon black presents several impurities, such as oxygen or sulphur [17], leading to a better dispersion inside the matrix. The corresponding piezoresistive response exhibits therefore a better stability in time. This is the reason why this filler is widely used when making piezoresistive sensor [6, 21, 22]. On the other hand, we can observe that the Martens Plus, while not perfect, expectedly exhibits a better stability regarding creep.

The same experiment was performed on aluminum with 12% vol. of graphite in Epotek 377 as a matrix. The results are reported in Fig 7. At room temperature, the GF_L values change dramatically on the aluminum substrate, due to instability during the measurement and the aluminum ductility. When the weight is put on the beam tip, a higher strain is exerted than on alumina. If we now consider the effect of temperature, the tendency is the same as on alumina substrate: we can see that the signal observed on aluminum shows strong instabilities when the temperature is raised close to the T_g range. The effect is even increased, due to the fact that the thermal expansion of the epoxy on aluminum is higher.

4. Conclusion

The piezoresistive response of thick-film epoxy-graphite composite materials was studied on two different substrates: alumina and aluminum. We demonstrate that particle size has a somewhat more important effect than in resistivity measurements, due to the tunneling effect. We also once more highlighted the role of T_g on mechanical stability, which sets the application temperature ceiling, as the material will dilate and rapidly relax around this temperature. Both of these effects were verified on aluminum substrate and were even amplified due to aluminum thermal expansion. Finally, creep was observed at different temperatures. We can see that even at room temperature, the higher T_g epoxy, though not perfect, presents better stability in time. These results are therefore promising for application to low-cost mechanical sensors. Additionally, functionalizing the graphite surface to achieve better cohesion with the epoxy may further improve stability.

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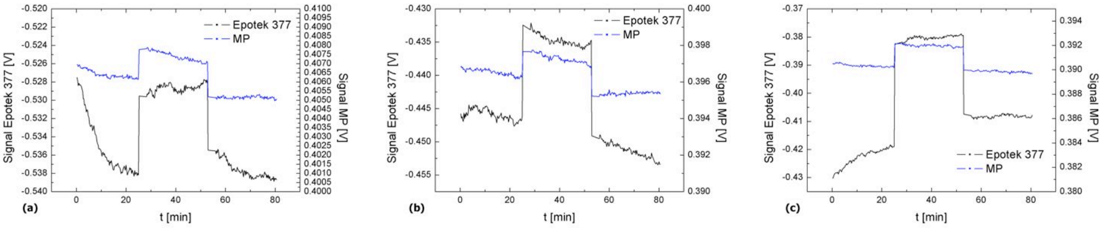

Fig 6. Signal vs. time for 12% vol of graphite in Epotek 377 and Martens Plus at 25°C (a), 50°C (b) and 80°C (c)

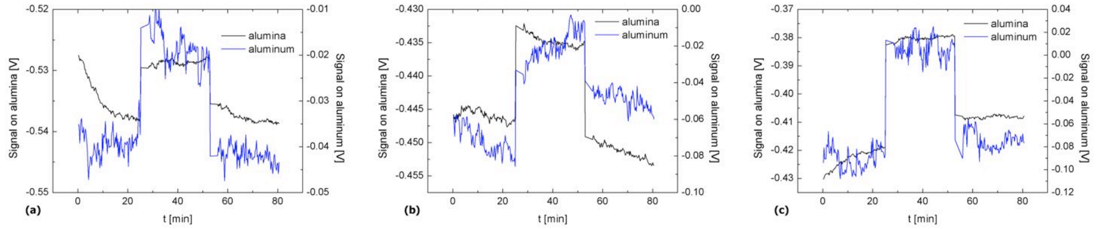

Fig 7. Signal vs. time for 12% vol. of graphite in Epotek 377 on alumina and aluminum substrate at 25°C (a), 50°C (b) and 80°C (c)

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Biographies

Nathalie Serra graduated in September 2007 (master degree in chemistry) at the "École Nationale Supérieure de Chimie de Lille" which is part of the French "Grandes Ecoles" network, and is pursuing a PhD in resistive nanocomposites at the EPFL.

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Peter Ryser received a Master degree in Physics (University Neuchâtel 1979), a PhD in applied Physics (University Geneva 1985) and a Masters Degree in Corporate Management (Lucerne 1993). His professional background includes several R&D activities. From 1990-1998 he was the head of research at Siemens Building Technologies. Since 1999 Peter Ryser is Professor at the Swiss Federal Institute of Technology EPFL in Lausanne and act as a director for the micro engineering section.